CERTIFICATION OF APPROVAL

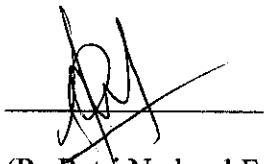
Fenton and Photo-Fenton Oxidation Process on Batik Making Effluents

by

Zakuan Bin Zaidi

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

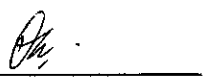


(Pn Putri Nadzrul Faizura Megat Khamaruddin)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2004

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



(ZAKUAN BIN ZAIDI)

ABSTRACT

Wastewater generated from batik making industry contains organics dyes. Dyes are listed in the Environment Quality Act 1974 as schedule waste. Thus, it is imperative to treat the wastewater. In this project, Fenton reaction is used to treat the wastewater from the batik making factory. Initial analysis was done for the wastewater and the characteristics of the wastewater were identified before proceeding with the experimental procedure. Two characteristics of waste water was monitored which are the Chemical Oxygen Demand (COD) and the color changes. The COD reading was taken by using HACH method 8000. The COD reading was measured in mg/L COD and the color was measured in term of its appearance and changes. For the reaction, two parameters were fixed which are the pH and the temperature. pH is fixed at 5, whereas the temperature was fixed at 30°C. Fenton reaction used two types of chemicals, which are $FeSO_4$ and H_2O_2. The chemicals are the variable parameters in these experiments because we vary the doses of the reagent. The chemicals were mixed to a blended reagent according to the ratio needed. The efficiency of the treatment is determined by varying the ratio of Fe: H_2O_2. The decreasing value of the COD and diminished color was monitored to see the process efficiency. Comparison of the efficiency was also determined between exposing the treatment process to radiation of light and keeping it in dark environment. Under light source radiation experiment is called photo-Fenton experiment, meanwhile for dark environment experiment is called Fenton experiment. It was found that the ratio of 1: 25 of photo-Fenton gives the best efficiency. Exposing the process to light showed better process efficiency.

ACKNOWLEDGEMENTS

In the name of ALLAH the most merciful, for blessing and giving me strength and ability to complete this thesis.

Firstly, I would like to acknowledge my deepest gratitude to my supervisor, Pn Putri Nadzrul Faizura Megat Khamaruddin for her expert guidance, constant attention, valuable suggestions, enthusiastics support and personal concern during the research and through out the course of my study. Thank you for providing me with 'a shoulder to cry on'. Enormous appreciation also goes to my Final Year Research Project Co-Ordinator, Miss Yuliana for your undivided attention as well as moral support and help rendered that guided me to finish my thesis.

Special thanks to the Head of Programme, Department of Chemical Engineering, Dr Hilmi Mukhtar for his permission to let we the final year students use all the brilliant and high technology facilities and equipments in completing our project. The quality leadership of his creates a healthy learning environment in completing our project. I would also extend my sincere appreciation for all the lecturers in the school that always gave me supports and guidance especially Pn Norhayati Mellon, Pn Anis Suhaila Shuib, Mr Khalik Mohd Sabil, and other lecturers as well.

My deepest gratitude to all the technicians and administrative staffs of Department of Chemical Engineering, UTP, especially to Mr Zaaba, Mr Jelani, Mr Sahar, and Mr Fauzi. for their warm help and guidance. To Mr Firdaus, thanks for being my friend during my Final Year Research Project. I would also thank University Technology of PETRONAS (UTP) for my placement here since January 2000.

Special appreciation goes to my ever-loving parents who always are on my side, Zaidi b. Mahzain and Zakiah bt. Hj. Morshidi, riding along with me on my ups and downs as well as giving me the encouragement to pursue my dreams. Not to forget, my relatives who always be there for me through my thick and thin. And a person who always give me courage and faith in my life, Dahlia bt Sani. You always in my heart. Love you all.

To my dear friends, Hanif, Malik, Johan, Akhdiad, Idzamani, Sylvia, Marlinne, Naizatul Husna, Fadzil, Violet, Mesye, Philips, Aizul, Diana, Dexter, Shah, Mukhrizan, and all close member of me in Village 4A, thanks for making my stayed in UTP so colorful and enjoyable. I would also extend my appreciation to all my friends, wherever they are. Thanks for being my friends.

May ALLAH bless all of us and only HE, The Almighty could repay all my debts to all of you.

Wassalamualaikum warahmatullah wabarokatuh

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND NOMENCLATURES

M	Molar
Ppm	Parts per million
mg/L	Milligrams per liter
dm^3	densimeter cubic
SSF	Solid State Fermentation
COD	Chemical Oxygen Demand
wt/wt	weight/weight
°C	degrees celcious
ml	Mililiter
nm	nano meter
wt/vol	weight/ volume
µL	micro liter

CHAPTER 1
INTRODUCTION

1.1 BACKGROUND STUDY

1.1.1 Importance of Advanced Oxidation Process (AOP)

Water treatment that exists nowadays cannot treat and amend all type of chemical compounds that are hazardous to the environment. Some studies that were developed in previous research proved significantly that pre-treatment by chemical oxidation will enhance greatly the detoxification and biodegradation of the wastewater or effluents generated by industries before releasing it to the municipal wastewater treatment plant. Thus, new technologies known as Advanced Oxidation Process (AOP) was developed to meet the requirements and supports what other wastewater treatment cannot do.

AOP have been studied and implemented by some parties such as ozonation, H_2O_2 photo catalysis, TiO_2 photo catalysis, and Fenton reagent. Fenton reagent is a type of treatment which using mixture of iron (Fe) and hydrogen peroxide (H_2O_2) at certain ratio to reduce and amend the organic contents in wastewater.

1.1.2 Fenton Process

Through development in the research, the studies made proved that using near UV/ visible radiation improved the rate of removal of organic pollutants and the extent of mineralization using Fe^{2+} / H_2O_2 and Fe^{3+} / H_2O_2 reagents or also known as Fenton reagent. Factors that contribute to efficiency of Fenton reagent

with UV/ visible radiation are photo reduction of Fe^{3+} and efficient use of light quanta.

Fenton process can be carried out in two ways, Fenton process and photo-Fenton process. Fenton process was conducted using Fenton reagent in dark environment. Meanwhile, photo-Fenton process was conducted using Fenton reagent under radiation of light.

1.1.4 Hazardous Content of Textile Industries Effluent

Waste water from dyeing and finishing industries is dangerous and harmful to the environment and human health. The organics can cause irritation to human skins and develop itches on the skin. The contents are characterized by high levels of chemical and biochemical oxygen demand, color, concentration of suspended solids and so on. What caused most of the difficulties was the reduction of color produced by residual dye. For such purposes, basically water treatment like coagulation, adsorption, reverse osmosis, chemical oxidation, and biological treatments were used at present time.

1.2 Problem statement

The bleaching effluents that produced by textile industries was generated in a very large volumes and contain clearly hazardous quantities of organic compound and chemical components that cannot easily treated by present chemical or biological treatments. Many textile industries are not aware or take for granted this crucial matter. Accidental release and discharge of this effluent in large quantities to environment can cause serious risk to the environment and human health as stated above.

1.3 OBJECTIVES AND SCOPE OF STUDY

- To investigate the efficiency of Fenton reagent to remove the hazardous compounds in the textile industries generated effluents.
- To determine the optimum ratio of H_2O_2 and Fe^{2+} concentration.
- To see the results of using Fenton and photo-Fenton reagent with the availability of light and irradiation, pH and temperature as constants parameter and iron (Fe) and H_2O_2 concentration as variables parameters.

1.3.1 Feasibility of Project within Scope and Time Frame

This project is significant as there are two types of experiments involved. The experiments are conducted using Fenton and photo-Fenton reagents. These two experiments were conducted on the same basis, to ensure that we can make a precise and quality comparative between two of them within specified scope. The procedure to carry out the experimental have been discussed with the Supervisor in charge and defined with laboratory technicians. Time frame given to students expects that all experiments should be carried out by mid semester before we proceed to the data analysis, detailed comparative study and report presentation.

CHAPTER 2

LITERATURE REVIEW

2.1 Textile industries wastewater characteristics

Textile industries generate wastewaters from bleaching process such as soaking the textile in water after coloring it with dye. The parameters of wastewater and their characteristics are configured approximately.

Table 1: Textile industries wastewater characteristics

Parameter	Maximum level
Ph	11
Initial dye concentrations	2.9×10^{-5} to 2.3×10^{-4} M
Chemical Oxygen Demand	450
Aspect	Red blue strong colored
Odor	Detergent scent
Total Suspended Solid	> 3500 ppm
Emulsion	No sedimentation tendency

(Source: Montserrat et al, 2001)

2.2 Advanced oxidation process (AOP)

The purpose of all Advanced Oxidation Process (AOP), is to produce hydroxyl radicals ('OH), a highly reactive oxidizing agent that reacts with and destroys most organic

pollutants in water. There are a variety of advanced oxidation approaches commercially available. Each has a scope of wastewater treatment applications that it is best suited for.

2.3 Comparison of treatment technologies of textile dyes removal

Textiles industries including batik making industries in Malaysia consume large volumes of water and chemicals for the wet processing. Considering both volumes discharged and effluent composition, the waste water generated by the textile industry is rated as the most polluting among all industrial sectors.

The release of dyes into waste waters by various industries poses serious environmental problems due to various dyes persistent and recalcitrant nature. Textile industries are responsible for the discharge of large quantities of dyes into natural waterways due to inefficiencies in techniques. Up to 50% of dyes maybe lost directly into waterways when using reactive dyes.

The presence of dyes in effluent is easily detectable even when released in small concentrations. Dye molecules consist of a chromagen, as an example an aromatic structure absorbing visible light, which anchors the dye into or within the fiber. There are about 12 classes of chromogenic groups, the most common being the azo type which makes up to 60-70% of all textile dyestuffs produced, followed by anthraquinone type. A second classification of dyes is based on their mode of application to textiles and distinguishes acid, reactive, metal-complex, disperse, vat, mordant, direct, basic and sulfur dyes (M.A Haroun et al., 2003)

Research on textiles effluent decolourization has often focused on reactive dyes for three reasons. First, reactive dyes represent an increasing market share, currently about 20-30% of the total market for dyes, because they are used to dye cotton, which makes up about half of the world's fiber consumption. Second, a large fraction, typically around

30% of the applied reactive dyes is wasted because of the dye hydrolysis in alkaline dye bath. As a result, dye house effluents typically contain 0.6-0.8 g dye dm^3. Third, conventional waste water treatment plants, which rely on sorption and aerobic biodegradation, have a low removal efficiency for reactive and other anionic soluble dyes, which leads to colored waterways, and public complaints (M.A Haroun et al., 2003)

Table 2: Current textile dyes treatments method advantages and disadvantages

Physical/ Chemical methods	Advantages	Disadvantages
Fenton's reagent	Effective decolourization of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 mins)
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Photochemical	No sludge production	Formation of by products
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removes all dyes types	Concentrated sludge production
Ion exchange	Regeneration: no absorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved oxygen
Electrokinetic's coagulation	Economically feasible	High sludge production

(M A Haroun, et al., 2003)

These methods that are widely used for removal of dye can be divided into three categories: chemical, physical, and biological. Currently the main methods of textile dye treatment are by physical and chemical means with research concentrating on cheaper effective alternatives (as shown in Table 2). Further explanation on the method of the treatment is explained in further sub-section 2.31, 2.32, and 2.33.

2.3.1 Chemical treatments

Oxidative process

This is the most commonly used method of decolourization by chemical means. This is mainly due to its simplicity of application. The main oxidizing agent is usually hydrogen peroxide (H_2O_2). This agent needs to be activated by some means, for example, ultra violet light. Many methods of chemical decolourization vary depending on the way in which the H_2O_2 is activated. Chemical oxidation removes the dye from the dye containing effluent by oxidation resulting in aromatic ring cleavage of the dye molecules (Raghavacharya, 1997)

Fenton's reagent (H2O2 + ferrous iron)

The Fenton's reagent works by oxidizing ferrous to ferric iron with simultaneous splitting of H_2O_2 into hydroxide ion and hydroxyl radicals. The latter oxidizes the dye while the former precipitates with ferric iron together with organics. One major disadvantage of using this method is sludge generation through the flocculation of the reagent and the dye molecules. The sludge, which contains the concentrated impurities, still requires disposal. It has conventionally been incinerated to produce power, but such disposal is seen by some to be far from environmentally friendly.

Ozonation

Ozone is a very good oxidizing agent due to its high instability compared to chlorine, another oxidizing agent and H_2O_2. It can decolorizes all dyes, except for non-soluble disperse and vat dyes which react slowly. Ozone is less efficient with high strength raw textile waste water, thus it is advisable to use ozone only as final treatment or at least following chemical coagulation (Strickland et al., 1995).

One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of waste water and sludge. A disadvantage of ozonation is its short half-life, typically being 20 minutes. This time can be further shortened if dyes are present, with stability being affected by the presence of salts, pH, and temperature. Better results can be achieved using irradiation or with a membrane filtration technique. One of the major drawbacks with ozonation is cost; continuous ozonation is required due to its short half-line (Xu et al.., 1999)

Photo catalysis

UV light has been tested in combination with H_2O_2 or solid catalysts such as TiO_2 for decolourization of dye solutions. This method degrades dye molecules to CO_2 and H_2O by UV treatment in the presence of H_2O_2. Degradation is caused by the production of high concentrations of hydroxyl radicals. UV light may be used to activate chemicals, such as H_2O_2, and the rate of dye removal is influenced by the intensity of the UV radiation, pH, dye structure and the dye bath composition. (Davis, 1994; Reeves, 1992)

Sodium hypochloride (NaOCl)

This method attacks at the amino group of the dye molecule by the Chlorine$^+$ (Cl^+). It initiates and accelerates azo-bond cleavage. This method is unsuitable for disperse dye. An increase in decolourization is seen with an increase in Cl concentration. The use of Cl for dye removal is becoming less frequent due to the negative effects it has when

released into waterway and the release of aromatic amines which are carcinogenic, or otherwise toxic molecules (Banat, 1999).

Electrochemical destructions

This is a relatively new technique, which was developed in the mid 1990s. It has some significant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge build up. The breakdown metabolites are generally not hazardous leaving it safe for treated waste waters to be released back into waterways. It shows efficient and economical removal of dyes and a high efficiency for color removal and degradation of recalcitrant pollutants. Relatively high flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to the price of chemicals (M.A Haroun et al., 2003).

2.3.2 Physical treatments

Adsorption

Adsorption technique has gained favor recently due to their efficiency in the removal of pollutants too stable for conventional methods. Adsorption produces a high quality product, and is a process, which is economically feasible. Decolourization is a result of two mechanisms: adsorption and ion exchange, and is influenced by many physio-chemical factors, such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time (Kumar, 1998).

Activated carbon

This is the most commonly used method of dye removal by adsorption and is very effective for adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent, dispersed, direct, vat, pigment, and reactive dyes. Performance is dependent on the type

of carbon used and the characteristics of waste water. Removal rates can be improved by using massive doses, although regeneration or reuse results in a steep reduction in performance, and efficiency of dye removal become unpredictable and dependent on massive doses of carbon. Activated carbon, like many other dye removal treatments, is well suited for one particular waste system and ineffective in another. Activated carbon is expensive. The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered. In addition to this reactivation, it also results in 10 - 15% loss of sorbent (M.A Haroun et al., 2003).

Peat

The cellular structure of peat makes it an ideal choice as an adsorbent. It has the ability to adsorb transition metals and polar organic compounds from dye containing effluents. Peat may be seen as a viable adsorbent in countries such as Ireland and UK, where it is widely available. Peat requires no activation, unlike activated carbon, and also costs much less. Due to activated carbon's powdered nature, it has a much larger surface area, and hence has a better capacity for adsorption. Spent peat may be burned and utilized for steam rising, or potentially, as substrate in solid state fermentation (SSF), for protein enrichment. The other methods of physical treatment is wood chips, fly ash and coal (mixture), silica gel, membrane filtration, ion exchange, and electrokinetic's coagulation (Poots et al., 1976).

2.3.3 Biological treatments

Anaerobic bioremediation systems

Anaerobic bioremediation allows azo and other water soluble dyes to be colorized. This decolourization involves an oxidation reduction reaction with hydrogen rather than free molecular oxygen in aerobic systems. Typically, anaerobic breakdown yields methane and hydrogen sulphide.

Anaerobic degradation of textile dye yields only azo reduction. Mineralization doesn't occur. It has been shown that azo and nitro components are reduced in the sediments and in the intestinal environment, resulting in the regeneration of the parent toxic amines. A major advantage of this anaerobic system, apart from the decolourization of soluble dyes, is the production of biogas. Biogas can be reused to provide heat and power, and will reduce energy costs (M.A. Haroun et al., 2003).

Adsorption by living or dead microbial biomass

The uptake or accumulation of chemicals by microbial mass has been termed biosorption. Dead bacteria, yeast and fungi have all been used for the purpose of decolorizing dye containing effluents.

Textile dyes vary greatly in their chemistries, and therefore their interactions with micro-organisms depend on the chemistry of a particular dye and the specific chemistry of the microbial biomass. It can be said that certain dyes have a particular affinity for binding with microbial species. It had been observed that biomass derived from the thermo tolerant ethanol producing yeast strain, exhibited a relatively high affinity for heavy metals (M.A. Haroun et al., 2003).

Decolourization by white-rot fungi

White-rot fungi are those organisms that are able to degrade lignin, the structural polymer found in woody plants. This fungus is capable of degrading dioxins, polychlorinated biphenyls and other chloro-organics. White-rot fungi are able to degrade dyes using enzymes, such as lignin peroxidases, manganese dependent perioxidases. Although white-rot fungi have been shown to decolorize dyes in liquid fermentations, enzyme production has also been shown to be unreliable. This is mainly due to the unfamiliar environment of liquid fermentation. The ability to utilize these fungi in their natural environment means that they are more likely to be more effective in solid state fermentation (SSF) (Reddy, 1995).

2.4 Mechanisms of Fenton's reagent

Many metals have special oxygen transfer properties which improve the utility of hydrogen peroxide. By far, the most common of these is iron which, when used in the prescribed manner, results in the generation of highly reactive hydroxyl radicals (·OH). The reactivity of this system was first observed in 1894 by its inventor H.J.H Fenton, but its utility was not recognized until the 1930's once the mechanisms were identified. Today, Fenton's reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (phenols, formaldehyde, BTEX, and complex wastes derived from pesticides, wood preservatives, plastics additives, and rubber chemicals).

This process may be used to wastewater, contaminated soils and sludge with the following action. Two or three of the functions of this reagent are applied in this project, which is to remove the COD, odor and color.

In this experiment, after addition of the iron and the hydrogen peroxide, they are going to react together to generate some hydroxyl radicals as it shows in the following equations. Following reactions depicts the reaction between iron ion and hydrogen peroxide. As can be see it generates hydroxyl radical that is important to degrade the organics dyes in the wastewater.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad \text{.....Equation 1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^+ \quad \text{.....Equation 2}$$

Reaction rates with Fenton's reagent are generally limited by the rate of ·OH generation and less so by the specific wastewater being treated. Typical Fe: H_2O_2 ratios are 1:5-10 wt/wt, though iron levels less than 25-50 mg/L can require excessive reaction times (10-24 hours). This is particularly true where the oxidation products (organic acids)

sequester the iron and remove it from the catalytic cycle. Fenton's reagent is most effective as a pretreatment tool, where COD's are more than 500 mg/L. This is due to the loss in selectivity as pollutant levels decrease:

$\cdot OH + H_2O_2 \rightarrow \cdot O_2H+$ .....Equation 3

$\cdot OH + Fe^{3+} \rightarrow Fe^{2+} + OH^-$ .....Equation 4

The equation showed above is the extent of the reaction after generation of hydroxyl radical.

In addition to free radical scavengers, the process is inhibited by (iron) chelants such as phosphate, EDTA, formaldehyde, and citric/oxalic acids. Sensitivity of Fenton's reagent to different wastewaters is not the same. Thus it is recommended that the reaction always be characterized through laboratory treatability tests before proceeding to plant scale (Lenntech, 2003)

2.4.1 Hydroxyl radical reactivity

The hydroxyl radical is one of the most reactive chemical species known. The chemical reactions of the hydroxyl radical in water are of four types:

Addition: $\cdot OH + C_6H_6 \rightarrow (OH)C_6H_6$
where the hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form radical product.

Hydrogen Abstraction: $OH + CH_3OH \rightarrow \cdot CH_2OH + H_2O$
Where an organic free radical and water are formed

Electron transfer: $OH + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^-$

where ions of a higher valence state are formed, or an atom or free radical if a mononegative is oxidized.

Radical interaction: $\cdot OH + \cdot OH \rightarrow H_2O_2$
where the hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product.

In applying Fenton's reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanisms (hydrogen abstraction and oxygen addition) predominate. Typical rates of reaction between the hydroxyl radical and organic materials are $10^9 - 10^{10}$ k ($M^{-1}s^{-1}$).

2.4.2 Effect of iron concentration

In the absence of iron (Fe), there is no evidence of hydroxyl radical formation when, for example, H_2O_2 is added to a phenolic wastewater (no reduction in the level of phenol occurs). As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes inefficient. This feature (an optimal dose range for iron catalyst) is characteristic of Fenton's reagent, although the definition of the range varies between wastewaters. Three factors typically influence its definition:

1. A minimal threshold concentration of 3-15 mg/L Fe which allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material.

2. A constant ratio of Fe: substrate above the minimal threshold, typically 1 part Fe per 10 -50 parts substrate, which produces the desired end products. Note that the ratio of Fe: substrates may affect the distribution of reaction products.

3. A supplemental aliquot of Fe which saturates the chelating properties in the wastewater, thereby unsequestered iron to catalyze the formation of hydroxyl radicals.

Iron dose may also be expressed as a ratio to H_2O_2 dose. Typical ranges are 1 part Fe per 5-25 parts H_2O_2 (wt/wt) (Lenntech, 2003).

2.4.3 Effect of iron type (Ferrous or Ferric)

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction. The catalytic cycle begins quickly if H_2O_2 and organic material are in abundance. However, if low doses of Fenton's reagent are being used, some research suggests ferrous (Fe^{2+}) iron may be preferred. Neither does it matter whether a chloride or sulfate salt of the iron is used, although with the former, chlorine may be generated at high rates of application.

It is also possible to recycle the iron following the reaction. This can be done by raising the pH, separating the iron floc, and re-acidifying the iron sludge. There have been some developments in supported catalysts that facilitate iron recovery and reuse.

2.4.4 Effect of H_2O_2 concentration

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory for each waste to be treated. For example, in a typical application the following series of reaction will occur:

Substrate → oxidized intermediate A → oxidized intermediate B → oxidized intermediate C → oxidized intermediate D → oxidized intermediate E → CO_2

Each transformation in this series has its own reaction rate and, as the case of phenolic illustrates, there may occur build up of an undesirable intermediate (quinones), which requires sufficient H_2O_2 to be added to push the reaction beyond that point. This is frequently seen when pretreating a complex organic wastewater for toxicity reduction. As the H_2O_2 dose is increased, a steady reduction in COD may occur with little or no in toxicity until a threshold is attained, whereupon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity (Lenntech, 2003).

2.4.5 Effect of temperature

The rate of reaction with Fenton's reagent increases with increasing temperature, with the effect more pronounced at temperature more than 20°C. However, as temperatures increase above 40-50°C, the efficiency of H_2O_2 utilization declines. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. As a practical matter, most commercial applications of Fenton's reagent occur at temperatures between 20 -40°C.

Applications of Fenton's reagent for pretreating high strength wastes may require controlled or sequential addition of H_2O_2 to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when H_2O_2 doses exceed 10-20g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well (Lenntech, 2003)

2.4.6 Effect of pH

The optimal pH occurs between pH 3 and pH6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. There have been some recent developments using nonradical scavenging sequestering agents to extend the useful pH range to 8-9,

but no commercial applications are known. The drop in efficiency on the acid side is less dramatic given the logarithmic function of pH, and is generally a concern only with high application rates.

A second aspect of pH deals with its shift as the reaction progresses. First drop in pH is caused by the addition of $FeSO_4$ catalyst which typically contains residual H_2SO_4. A second, more pronounced drop in pH occurs as the H_2O_2 is added, and continues gradually at a rate which is largely dependent on catalyst concentration. This drop in pH is attributed to the fragmenting of organic material into organic acids. This pH change is often monitored to ensure that the reaction is progressing as planned. The absence of such a pH decreases may mean that the reaction is inhibited and that a potentially hazardous build-up of H_2O_2 is occurring within the reaction mixture.

In highly concentrated waste streams (more than 10g/L COD), it may be necessary to perform the oxidation in steps, readjusting the pH upwards to pH 4-5 after each step so as to prevent low pH from inhibiting the reaction (M.A. Haroun et al., 2003; E. G Solozhenko et al., 1995).

2.4.7 Effect of reaction time

The time needed to complete a Fenton reaction will depend on the many variables discussed above, most notably catalyst dose and wastewater strength. For simple phenol oxidation, typical reaction times are 30 – 60 minutes. For more complex or more concentrated wastes, the reaction may take several hours. In such cases, performing the reaction in steps (adding both iron and H_2O_2) may be more effective and safer than increasing the initial charges.

Determining the completion of the reaction may prove troublesome. The presence of residual H_2O_2 will interfere with many wastewater analyses. Residual H_2O_2 may be removed by raising the pH to 7-10, or by neutralizing with bisulfite solution. Often, observing color changes can use up as the reaction reaches completion (Lenntech, 2003).

2.4.8 Effect of post treatment

As a result of degrading complex organic materials into organic acid fragments, the pre-oxidized effluent is generally more amenable to conventional treatment, such as flocculation and biotreatment. The presence of iron in the reaction mixture makes it particularly suited to subsequent lime flocculation. In many cases, it may be possible to remove up to 80% of the wastewater COD through a combination of Fenton's reagent and lime flocculation. Significantly, this may be achieved with a H_2O_2 dose of 50-75% of the stoichiometry (Lenntech, 2003).

2.5 Mechanism's of photo-Fenton reagent

The process should be carried out by adjusting the pH of the wastewater to 3-5, then adding the iron catalyst (eg. $FeSO_4$). Then, slowly add H_2O_2. The pH should be monitored. Below is how the reactions described by equations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + .OH + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + .OOH + H^+$$

When exposed to UV irradiation, the compounds begin to decompose and will produce OH and Fe^{2+} ions:

$$Fe(OH)^{2+} \xleftarrow{uv} Fe^{2+} + \cdot OH$$

The net result of the application of the above reactions is that the organic contaminant is completely mineralized, meaning that it is converted to either carbon dioxide gas or water and mineral salt; all innocuous constituents. This ability to completely destroy contaminants is a major advantage of advanced oxidation over competing processes.

2.6 COD value and Environmental Quality Act 1974

COD stands for Chemical Oxygen Demand. In this experiment, the main indicator of the effectiveness of the experiment is the COD value. COD value of one sample reflects the concentration of the organic material that depends on oxygen. Thus, the oxygen will reduce as these organic materials are in large concentration. For this experiment, the targeted value of the COD after treatment or experiment is less than 100 mg/L as stated in Environmental Quality Act, 1974, on Environmental Quality (Sewage and Industrial Effluents) Regulations 1979.

CHAPTER 3
METHODOLOGY

3.1 PROJECT APPROACH

The following phase of research and development have been planned and identified to suits most for this project. These stages are important to ensure the project will be run smoothly and successfully before proceeding to the next steps. Basically, methodology can be divided into 5 main stages:

i. *Selection of project topics*: This first stage is crucial which it will lead to the successive progress of the project afterwards. Students should have confidence to complete the project in time frame given when choosing a topic.

ii. *Project planning:* All defined works and scopes were planned carefully with time frames and datelines. This is to ensure the smoothness of the project so that the students can complete the project on time.

iii. *Literature study:* Theory and information are gathered in this step. The overview or briefly view should be clear and the students know generally what they're doing. In this project, the basic knowledge to carry with this project is to know what are the Advanced Oxidation Process (AOP) and the applications of it in the experiments related.

iv. *Laboratory work:* This step need to be carried out with full preparation on the experiments and the information needed. Some experiments cannot be carried out repeatedly if failed because it can lag other tasks. In this project we will carried out experiments using Fenton, photo-Fenton, and Fenton-like reagents.

v. *Data analysis:* All experiments results and observation shall be documented for detailed discussion and analysis with Supervisor. Comparative study should be carried out since we will be doing two types of experiments.

3.2 Textile Industries Effluents Production

In this experiment, the samples were taken from a batik making factory, Kilang Batik Kam, situated at Tanah Hitam, Chemor. The factory was situated about 20 kilometers from Ipoh. At the premise, they have a show room and a factory where they produce batik textiles. A river was located at the back of the factory.

The samples was taken directly form their factory and also the downstream river. Below is the process flow of producing batik textiles and where effluents were produced.

1. Chanting- is where pattern are drawn on plain fabric (white color) using wax (liquid form).

2. Dyeing the fabric with desired colors.

3. The fabric is boiled in water together with sodium silicate to dye the color. There are two types of sodium silicate used, C140HP and C100HP. C140HP is diluted with water due to high concentration of sodium silicate contains. The sodium silicate used to boil the fabric is either one of the two types.

4. Then the fabric was soaked and washed in pond no. 1 for first wash. It was then soaked for second time in pond no. 1B. This process is mainly to remove the excess color after the dyeing process.

5. The fabric is then boiled again and this time with adding soda ash. This process was done to remove the wax which was used to draw the pattern in chanting process. This process takes place in pond no 2.

6. It was soaked again in pond no. 3A and second time in pond no. 3B. This process is mainly to remove and washed the excess wax.

7. Lastly, it was soaked in water added with fabric softener (Softlan) in pond no. 4, to soften the fabric.

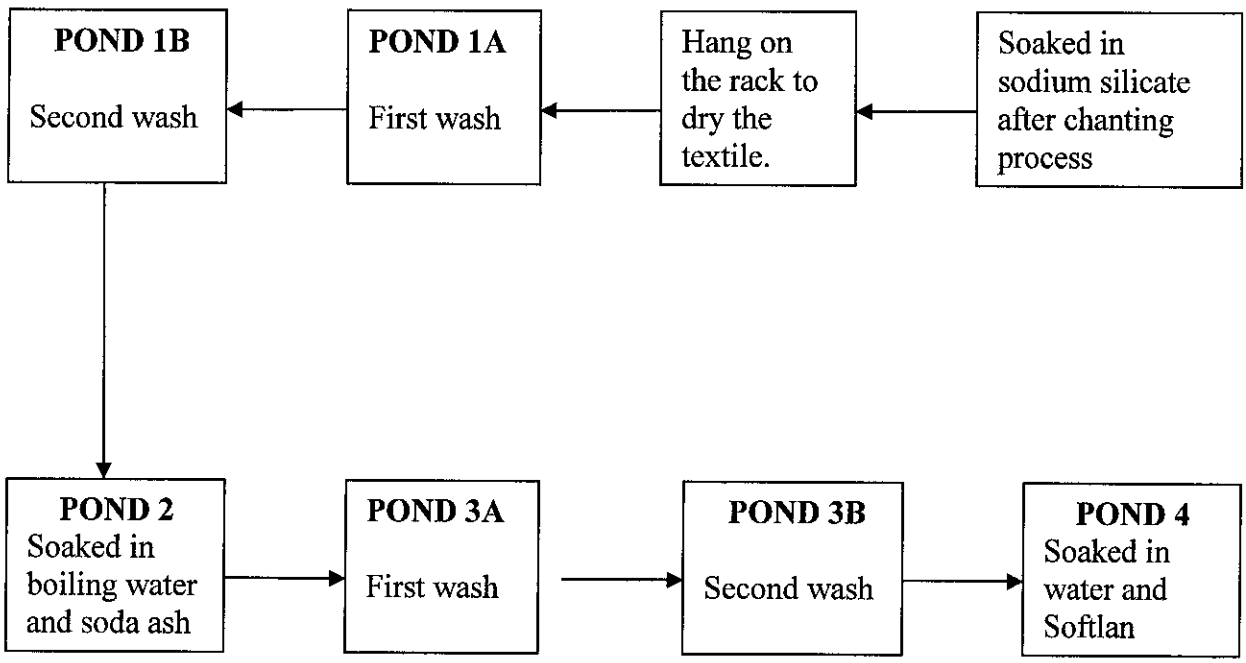


Figure 1: Process flow of batik making and effluents generation

3.3 Textile industries wastewater sampling procedure

Before the samples were taken, there are some precautions steps that have to be complying with. The steps were included in this procedure below:

1. Black bottle sample is used *(see figure 2)* to avoid the contact with sunlight (UV). This can affect the condition of the effluents before COD test procedure is carried out for initial effluents.

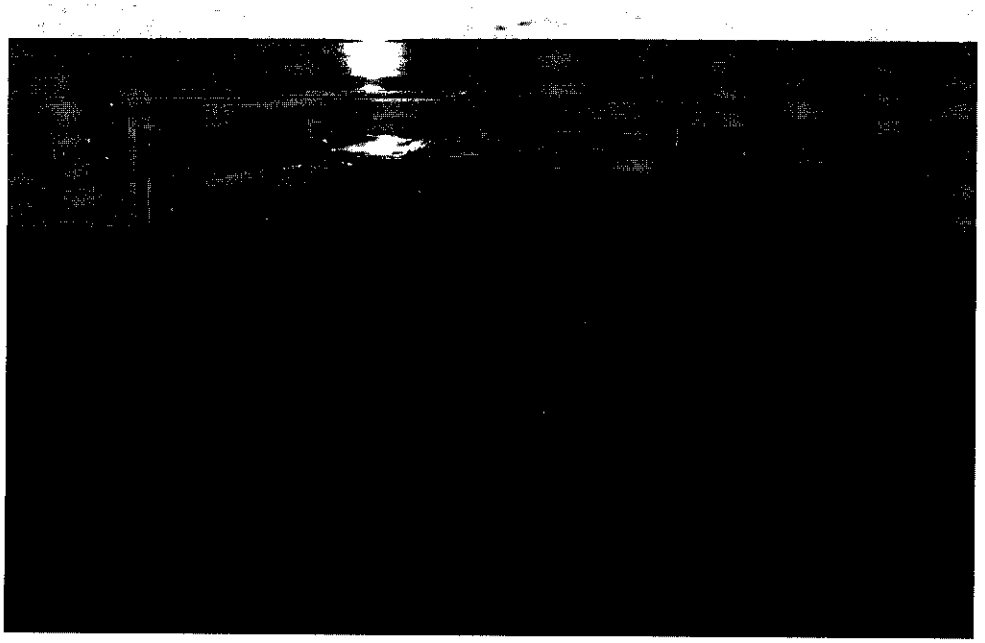


Figure 2: Sampling bottle

2. Effluents sample taken as normal procedure and placed in a cold box. Ensure that the cold box is maintained at low temperature degrees. When taking the samples, ensure that gloves are to be worn. The dyes concentration are harmful and hazardous and can irritate the skin if get into contacts.

3. Store the samples in a refrigerator at temperature around 4°C. Analysis should be done immediately because if the samples were stored long enough, it is afraid that the natures of the concentration will deflect from its origin.

3.4 Analysis for the initial contains of the samples

3.4.1 Preparing the samples for analysis

1. 800 ml sample were collected in a 1000 ml beaker. The effluents have to be filtered to eliminate the contents of wax and solids. This is to ensure the effectiveness of the experiment without outside factors affecting it.

2. The filtering apparatus was assembled. In this procedure, we use vacuum suction filtering equipment which consists of the filter paper (Whatman 1), filter holder, filter flask, and an aspirator.

3. The filter paper was rinse by pouring about 50 ml of distilled water through the filtering apparatus. The rinse water was then discarded.

4. An amount of 50 ml of effluents was poured through the filter.

5. The filtered effluents were stored in another storage medium, clean and dark for the analysis.

6. Steps 1 to 5 were repeated for another bottle of the effluents.

3.4.2 Chemical Oxygen Demand (COD) procedures.

COD contents was determined by using HACH method 8000 which is approved by United States Environmental Protection Agency (USEPA).All precautions should be taken when handling this procedure. The reagent contains inside the vials are hazardous to human and other materials. Appropriate eye protection as goggles and clothing such as lab coat should be wear when handling this procedure.

Procedure to prepare the sample:

1. The waste water that has been filtered was mixed and stirs using magnetic stirrer and hot plate. The temperature was held constant at room temperature which was at 28°C. This is to ensure all the contents in the waste water are mixed thoroughly. If the samples are not mixed thoroughly, the reading of the COD may be not very precise.

2. The COD reactor was switched on and preheated to 150 °C before placing the vials inside. Plastic cover should be placed in front of the reactor.

3. COD vials used are the high range type. This type of vials contains reagent mixture that are specifically used to measures samples with high range of COD between 0 to 1,500 mg/l. The reagent mixture is light-sensitive. The unused vials have to be kept in the opaque shipping container.

4. Before pouring the samples into the vials, the milipipette was set to 2.00 ml. In this experiment, we are using the milipipette instead of using the ordinary pipette. This milipipette is more convenience and accurate. Prior using the milipipette, the plastic tip is rinsed with distilled water.

5. Pour in 2.00 ml of samples in to the vial. Three minimum replicates should be prepared and analyzed for the best results. When handling these vials, one should be careful not to spill the contents. This can affect the results and furthermore, it is hazardous to the skin and other materials.

6. The vial cap was replaced tightly. The tightness of the vial cap should be checked by observing if there any spillage occurs when we invert them gently. Gloves should be worn during this procedure. Outside part of the COD vial was rinsed with distilled water and wiped dry with clean towel.

7. The vial contents can be mixed up by inverting it gently several times. Then the vial was places inside the preheated reactor. Steps 4 to 7 were repeated for other samples.

8. For zeroing purpose, a blank sample was prepared. 2.00 mL of distilled water was added to a vial. The blank sample was placed in the COD reactor. Milipipette used for preparing the blank sample should clean enough without any contaminations.

9. All the vials are heated inside the COD reactor *(see figure 3)* for 2 hours. Make sure all vials are labeled to avoid any confusing situation happen.

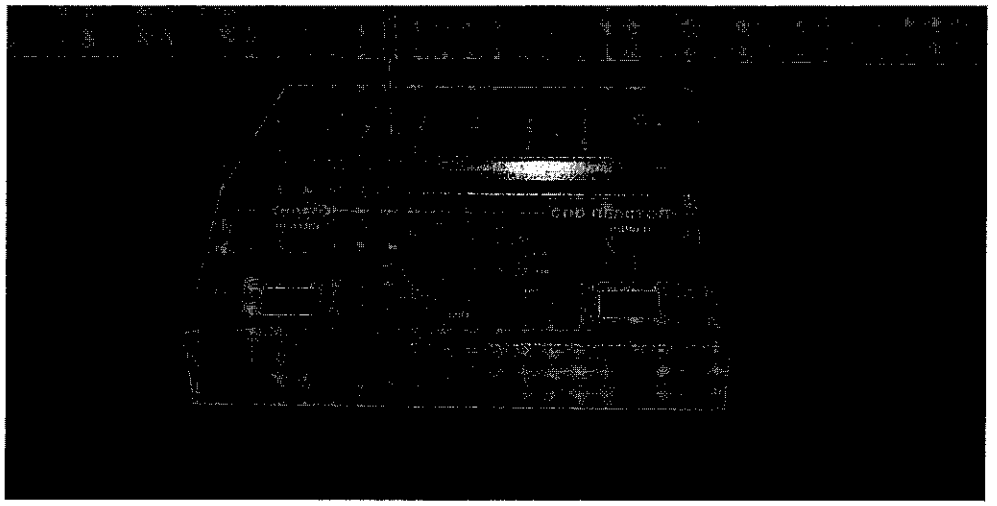


Figure 3: COD reactor

10. After 2 hours, the COD reactor was switched off and let the vials to cool down to room temperature.

11. The vials were inverted gently for several times while still warm. Place the vials into a rack. Let them to cool down to room temperature..

3.4.3 Procedure for testing the COD contents

1. Equipment used for testing the high range COD content is DR 4000 *(see figure4)*. There are many programs installed in this equipment. One of them is to test the high range COD content in samples prepared.

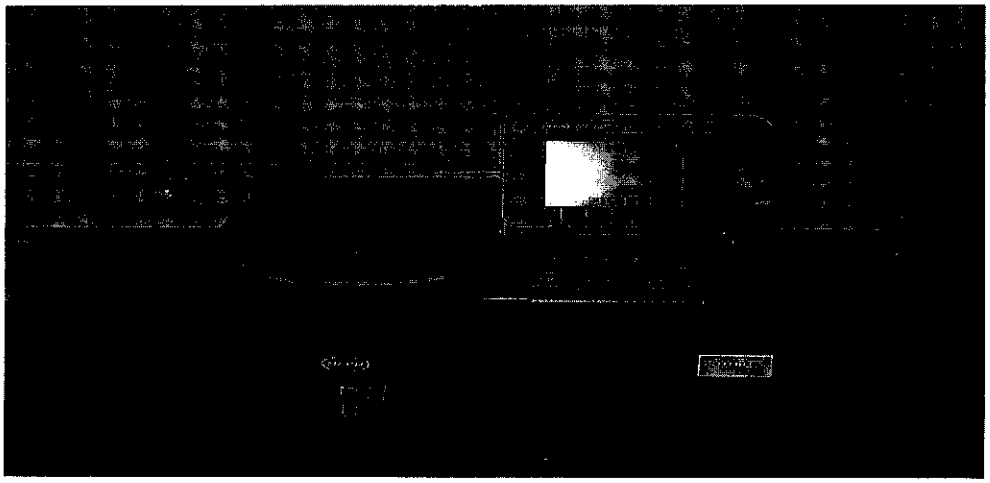


Figure 4: DR 4000 spectrophotometer

2. After the equipment is switched on, select program number 2720. The display will immediately show HACH PROGRAM: 2720 COD, HR, and HR PLUS. Then the wavelength was dialed to 620 nm automatically. If the wavelength does not appear as 620 nm, it has to be dialed manually.

3. The test tube adapter was inserted into the sample cell module by sliding it under the thumb screw and into the alignment grooves. The thumb screw should be fastened tightly.

4. The blank sample was taken out from the rack. The vial was wiped using a damp towel first, and then followed by a dry one. This is to ensure all the fingerprints and other marks are wiped away.

5. The blank was then placed into the adapter with its HACH logo facing the front of the instrument. The light shield then was closed.

6. The soft key under ZERO was pressed for zeroing purpose. The display will show 0 mg/l COD.

7. The sample was taken out from the rack. Wipe the vials using a damp towel first, and then followed by a dry one. This is to ensure all the fingerprints and other marks are wiped away.

8. The sample vial was placed into the adapter with the HACH logo facing the front of the instrument. The light shield was closed tightly. Step 7 to 8 were repeated for other samples

3.5 Preparations of Fenton's reagent

3.5.1 For Iron (Fe):

Amount of organics = 305 mg/L (after COD of initial effluents)

Amount of **Fe** needed:

305/10 = 30.5 mg/L (for specified volume needed at the minimal threshold of the ratio). Theoretically, minimal 3-15 mg/L Fe allows reaction to proceed within reasonable time regardless of organic waste concentration and the ratio of Fe: substrate above the minimal threshold, typically 1: 10-50 (wt/wt), produces the desired end products. In this experiment, the ratio of Fe: substrate of 1: 10 is adopted. That is why we divide the initial COD concentration of the effluents with 10.

We choose to take 30 mg/L because the initial amount was rounded from 30.5 mg/L to 30 mg/L for easier calculation.

Waste water amount in each experiment used = 150 mL

Amount of **Fe** to achieve concentration of 30 mg/L:

30 mg/L = x / 150 mL

x = 4.5 mg of **Fe** only

In this experiment, **$FeSO_4 \cdot 7H_2O$** is used. Therefore the total amount of **$FeSO_4 \cdot 7H_2O$** required to achieve 30 mg/L of Fe is considered as follows:

Molecular weight (MW) of **Fe** = 55.85 g

Molecular weight (MW) of **$FeSO_4 \cdot 7H_2O$** = 277.92 g

Weight of Fe only required = 4.5 mg

Thus, weight of **$FeSO_4 \cdot 7H_2O$** required to achieve concentration of 30 mg/L is:

= (MW $_{FeSO4 \cdot 7H2O}$ / MW **Fe**) x **Fe** required

= (277.92 x 10^3 mg / 55.85 x 10^3 mg) x 4.5 mg

= 22.4 mg of **$FeSO_4 \cdot 7H_2O$**

3.5.2 For H_2O_2:

Density of **H_2O_2** = 1.11 g/cm3 = 1110 mg/mL

The ratio for the reagent are **Fe : H_2O_2** = 1 : 5 (wt / wt), which means 4.5 mg of **Fe** : 22.5 mg of **H_2O_2**.

The available **H_2O_2** is in 30 % strength. This also equal to 30 g/100mL or 300 g/L.

30 % (wt / vol) of 1110 mg/mL **H_2O_2** is 333 mg/mL.

Thus, 1 mL of solution contains 333 mg of **H_2O_2** by weight. For the required 22.5 mg of **H_2O_2**;

Volume of **H_2O_2** = (22.5 mg / 333 mg) x 1 mL
= 0.068 mL
= 68 µL

Then, the calculations are simplified in the following table:

Table 3: Concentration of Fe and H_2O_2 at various ratio

Ratio of Fe : H_2O_2	Fe in mg	H_2O_2 in µL
1 : 5	22.4	68
1 : 10	22.4	135
1 : 15	22.4	203
1 : 20	22.4	270
1 : 25	22.4	338
1 : 30	22.4	405
1 : 35	22.4	473
1 : 40	22.4	541

3.6 Experimental procedures

3.6.1 Fenton's process experiment

Objective of the experiment:

1. To decrease the value of the initial COD contents in the samples.

2. To detect the changes of color of the samples.

Parameters:

Environment: Dark, no lights.

Constant: pH at 3-5

Temperature at 30°C

Variable: Concentration of H_2O_2 and $FeSO_4$ based on the ratio calculated in part 3.4

Equipments:

Rotary shaker water bath *(see figure 5)*

Micro weight balance *(see figure 6)*

Milipipette and micropipette

pH meter *(see figure 7)*

Beakers (250 ml, 1000 ml)

Conical flask (250 ml)

Aluminum foils

Spatula

Stop watch

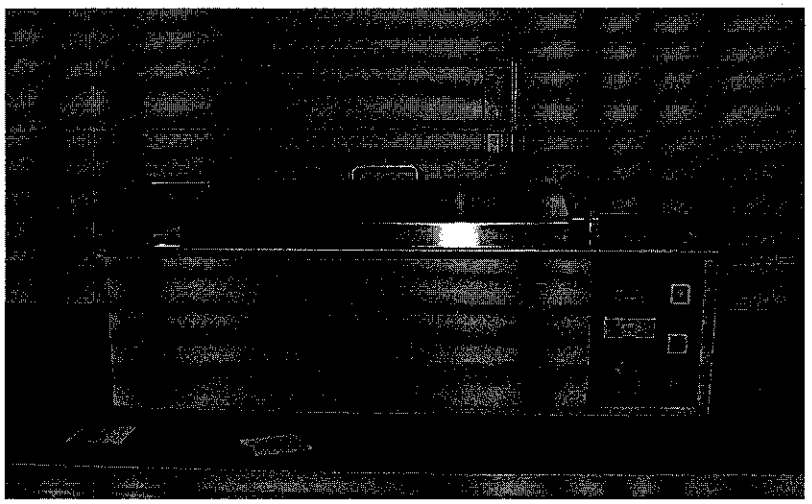


Figure 5: Rotary shaker water bath

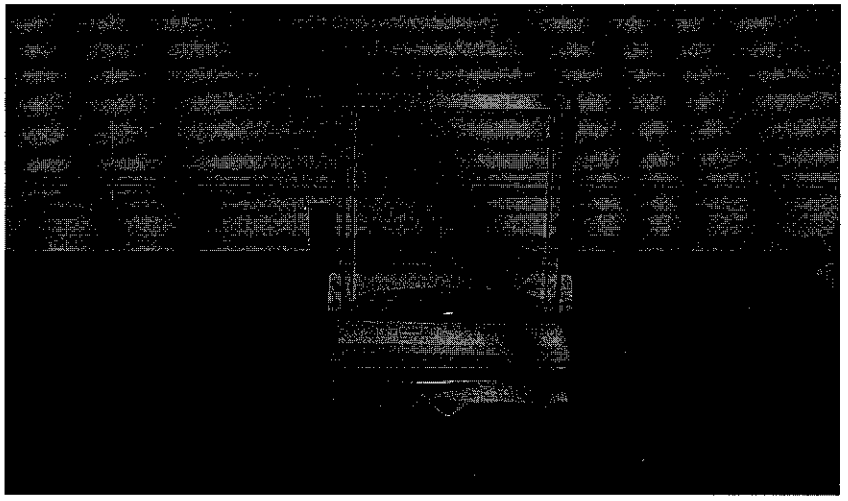


Figure 6: Micro weight balancer

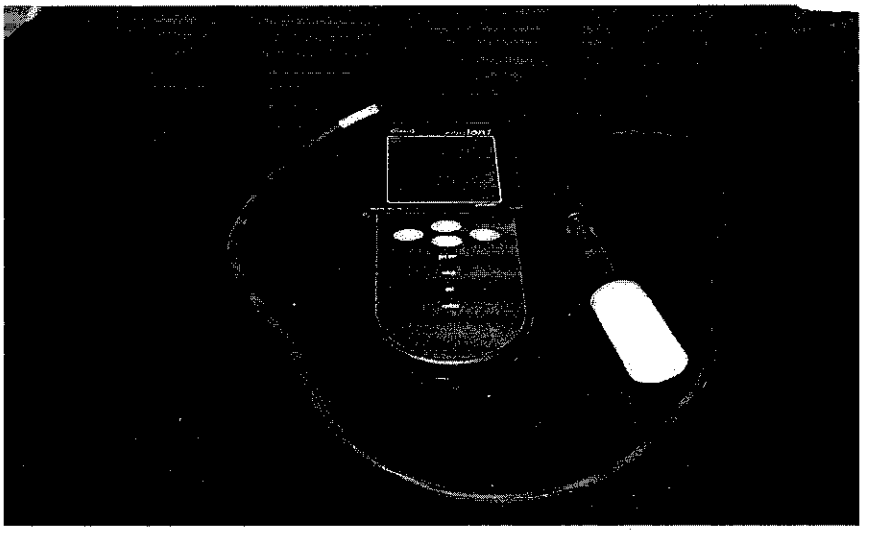


Figure 7: pH meter (sensION)

Chemicals:

$FeSO_4 \cdot 7H_2O$ (in powder form)

H_2O_2 (30 % concentrated)

H_2SO_4 (1 M)

Distilled water

Procedure:

Samples:

1. Waste water that has been filtered was poured into 1000 ml beaker in an amount of 500 ml.
2. The pH and temperature of the waste water was tested using pH meter.
3. H_2SO_4 was added to the wastewater to decrease the pH of the waste water to approximately 5.
4. After the pH is approximately at 5, stop step 3.

5. An amount of 150 ml of the waste water was poured into the conical flask. The conical flask was then put into the rotary shaker water bath with aluminum foils covering the flask's opening. Three numbers of samples for each ratio was prepared.
6. Set the rotary shaker water bath temperature to 30°C. Allow the temperature of the samples to stabilize.
7. Check the pH and temperature of the samples after 10 minutes.

Chemicals:

1. Volume of H_2O_2 and weight of $FeSO_4 \cdot 7H_2O$ was prepared according to the ratio of the experiment.
2. Using micro weight balancer, the weight of $FeSO_4 \cdot 7H_2O$ was weighted and the $FeSO_4 \cdot 7H_2O$ powder was put onto a filter paper.
3. Micro pipette was used to set the volume of H_2O_2 needed according to the ratio.

Experiment:

1. Recheck again the temperature and the pH before adding the chemicals.
2. Start the timer.
3. Switch on the shaker mode. Adjust the rotation to 80 rpm.
4. Pour in $FeSO_4 \cdot 7H_2O$ into the samples. Wait for 5 minutes. Take the pH and temperature reading. Record into the logbook.
5. Then, add slowly H_2O_2 into the samples. The H_2O_2 should be added every 5 minutes with a small amount until it finished. Take the pH and temperature reading every 5 minutes.
6. Allow the reaction to take place. Take pH and temperature reading every 5 minutes until one hour is accomplished.
7. Ensure that no light strikes into the samples because this set of experiment was conducted in dark.
8. Put the cover of the rotary shaker water bath and leave it for one day.

3.6.2 Photo-Fenton's process experiment

Objective of the experiment:

1. To decrease the value of the initial COD contents in the samples.

2. To detect the changes of color of the samples.

Parameters:

Environment: Available of light.

Constant: pH at 3-5

Temperature at 30°C

Variable: Concentration of H_2O_2 and $FeSO_4$ based on the ratio

Equipments:

Rotary shaker water bath
Micro weight balance
Milipipette and micropipette
Desk lamp (60 watt)
pH meter (sensION)
Beakers (250 ml, 1000 ml)
Conical flask (250 ml)
Aluminum foils
Spatula
Stop watch

Chemicals:

$FeSO_4 \cdot 7H_2O$ (in powder form)
H_2O_2 (30 % concentrated)
H_2SO_4 (1 M)
Distilled water

Procedure:

Samples:

1. Waste water that has been filtered was poured into 1000 ml beaker in an amount of 500 ml.
2. The pH and temperature of the waste water was tested using pH meter.
3. H_2SO_4 is added to the wastewater to decrease the pH of the waste water to approximately 5.
4. After the pH is approximately at 5, stop step 3.
5. An amount of 150 ml of the waste water was poured into the conical flask. The conical flask was then put into the rotary shaker water bath with aluminum foils covering the flask's opening. Three number of samples foe each ratio were prepared.
6. Set the rotary shaker water bath temperature to 30°C. Allow the temperature of the samples to stabilize.
7. Check the pH and temperature of the samples after 10 minutes.

Chemicals:

1. Volume of H_2O_2 and weight of $FeSO_4 \cdot 7H_2O$ was prepared according to the ratio of the experiment.
2. Using micro weight balancer, the weight of $FeSO_4 \cdot 7H_2O$ was weighted and the $FeSO_4 \cdot 7H_2O$ powder was put onto a filter paper.

3. Micro pipette was used to set the volume of H_2O_2 needed according to the ratio.

Experiment:

1. Recheck again the temperature and the pH before adding the chemicals.
2. Start the timer. Switch on the desk lamp light.
3. Switch on the shaker mode. Adjust the rotation to 80 rpm.
4. Pour in $FeSO_4$ into the samples. Wait for 5 minutes. Take the pH and temperature reading. Record into the logbook.
5. Then, add slowly H_2O2 into the samples. The H_2O_2 should be added every 5 minutes with a small amount until it finished. Take the pH and temperature reading every 5 minutes.
6. Allow the reaction to take place. Take pH and temperature reading every 5 minutes until one hour is accomplished.
7. Ensure that the light strikes to all the samples because this is a photo-Fenton process, a process using Fenton reagent, conducted with availability of light.
8. Leave open the cover of the rotary shaker water bath and leave it for one day.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Results and data analysis on the initial concentrations.

For the analysis of the initial contents of the effluents, the results for COD value are summarized as below:

Table 4: Initial COD value of the wastewater

Sample	COD value (mg/L)	Average COD value (mg/L)
sample 1	301	305
sample 2	304	
sample 3	310	

Sample – the effluents from each pond were mixed together with same ratio. It can be concluded from table 4 that the initial COD value of the effluents is 305 mg/L.

4.2 Fenton oxidation

4.2.1 COD reduction

The tables shown (Table 5 to Table 9) are the results obtained for Fenton's oxidation in term of COD concentration.

Table 5: Results for Fenton experiment with ratio (Fe: H_2O_2) of 1:5

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.24	29.5	5.24	29.5	5.25	29.5
5	4.42	29.5	4.47	29.5	4.43	29.5
10	4.38	29.5	4.43	29.5	4.36	29.5
15	4.33	30.0	4.36	30.0	4.34	30.0
20	4.32	30.0	4.36	30.0	4.34	30.0
25	4.32	30.0	4.36	30.0	4.34	30.0
30	4.32	30.0	4.35	30.0	4.34	30.0
35	4.32	30.0	4.35	30.0	4.34	30.0
40	4.31	30.0	4.35	30.0	4.33	30.0
45	4.31	30.0	4.35	30.0	4.33	30.0
50	4.31	30.0	4.34	30.0	4.33	30.0
55	4.31	30.0	4.34	30.0	4.33	30.0
60	4.29	30.0	4.34	30.0	4.31	30.0
COD	275		290		275	
Average COD	280					

Table 6: Results for Fenton experiment with ratio (Fe: H_2O_2) of 1:10

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.28	28.0	5.28	28.0	5.28	28.0
5	4.55	28.5	4.68	28.5	4.49	28.5
10	4.51	28.5	4.61	28.5	4.44	28.5
15	4.47	29.0	4.57	29.0	4.40	29.0
20	4.42	29.5	4.50	29.5	4.36	29.5
25	4.41	30.0	4.50	30.0	4.36	30.0
30	4.41	30.0	4.50	30.0	4.36	30.0
35	4.41	29.5	4.49	29.5	4.36	29.5
40	4.40	30.0	4.49	30.0	4.35	30.0
45	4.40	30.0	4.49	30.0	4.35	30.0
50	4.40	30.0	4.49	30.0	4.35	30.0
55	4.40	30.0	4.48	30.0	4.35	30.0
60	4.39	30.0	4.48	30.0	4.35	30.0
COD	250		260		228	
Average COD	246					

Table 7: Results for Fenton experiment with ratio (Fe: H_2O_2) of 1:15

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.23	29.5	5.23	29.5	5.23	29.5
5	4.39	29.5	4.44	29.5	4.38	29.5
10	4.35	29.5	4.40	29.5	4.35	29.5
15	4.30	29.5	4.35	29.5	4.31	29.5
20	4.27	30.0	4.32	30.0	4.28	30.0
25	4.25	30.0	4.32	30.0	4.24	30.0
30	4.25	29.5	4.32	29.5	4.24	29.5
35	4.25	30.0	4.31	30.0	4.24	30.0
40	4.25	30.0	4.31	30.0	4.24	30.0
45	4.24	30.0	4.31	30.0	4.23	30.0
50	4.24	30.0	4.31	30.0	4.23	30.0
55	4.24	30.0	4.30	30.0	4.23	30.0
60	4.24	30.0	4.30	30.0	4.23	30.0
COD	193		210		188	
Average COD	197					

Table 8: Results for Fenton experiment with ratio (Fe: H_2O_2) of 1:20

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.27	29.5	5.27	29.5	5.27	29.5
5	4.40	29.5	4.41	29.5	4.40	29.5
10	4.36	30.0	4.38	30.0	4.37	30.0
15	4.31	30.0	4.33	30.0	4.35	30.0
20	4.27	30.0	4.29	30.0	4.30	30.0
25	4.24	30.0	4.25	30.0	4.29	30.0
30	4.23	30.0	4.25	30.0	4.29	30.0
35	4.23	30.0	4.25	30.0	4.29	30.0
40	4.23	30.0	4.24	30.0	4.28	30.0
45	4.22	30.0	4.24	30.0	4.28	30.0
50	4.22	30.0	4.24	30.0	4.28	30.0
55	4.22	30.0	4.24	30.0	4.28	30.0
60	4.22	30.0	4.23	30.0	4.28	30.0
COD	138		145		164	
Average COD	149					

Table 9: Results for Fenton experiment with ratio (Fe: H_2O_2) of 1:25

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.20	29.0	5.20	29.0	5.20	29.0
5	4.37	29.0	4.41	29.0	4.39	29.0
10	4.33	29.5	4.37	29.5	4.35	29.5
15	4.30	29.5	4.35	29.5	4.32	29.5
20	4.26	29.5	4.31	29.5	4.29	29.5
25	4.24	30.0	4.28	30.0	4.25	30.0
30	4.23	30.0	4.28	30.0	4.25	30.0
35	4.23	30.0	4.28	30.0	4.25	30.0
40	4.23	30.0	4.27	30.0	4.25	30.0
45	4.23	30.0	4.27	30.0	4.24	30.0
50	4.22	30.0	4.27	30.0	4.24	30.0
55	4.22	30.0	4.27	30.0	4.24	30.0
60	4.22	30.0	4.27	30.0	4.24	30.0
COD	118		125		118	
Average COD	114					

The data shown in Table 5 to Table 9 are the results obtained from Fenton's oxidation experiment, for ratio (Fe: H_2O_2) of 1: 5 to 1:20 which was conducted in dark environment. The experiment was begun at initial pH of approximately 5.

Actually the pH setting was adjusted to achieve around pH 5. At first, the initial pH of the wastewater was at pH 11. It is in basic side. The pH was adjusted to pH 5.27 before the experimental procedure was carried out. The temperature was set at 30.0 degC for certain reason which will be discussed later. The pH was monitored to see the trend of the decreasing pH. It is also to ensure that the pH decreasing based on the theory applied. It can be seen that from the entire ratio, the COD value of the wastewater after the experiment was keep on decreasing. This success achievement was contributed from one among the factors, the decreasing in pH after the addition of the $FeSO_4$ and H_2O_2.

If we refer to the figure 8, the obvious decrease in pH was detected around minutes 0 to 5. Decreases also occur at minute 5 to 10 but it was too small. This decrease in pH was

occurred by the addition of $FeSO_4$ and H_2O_2. The theory was applied here where after addition of $FeSO_4$ and H_2O_2, the pH will decrease and then maintain at pH around 4 for the reaction to takes place. This figure is similar to all the of the Fenton oxidation experiments. .

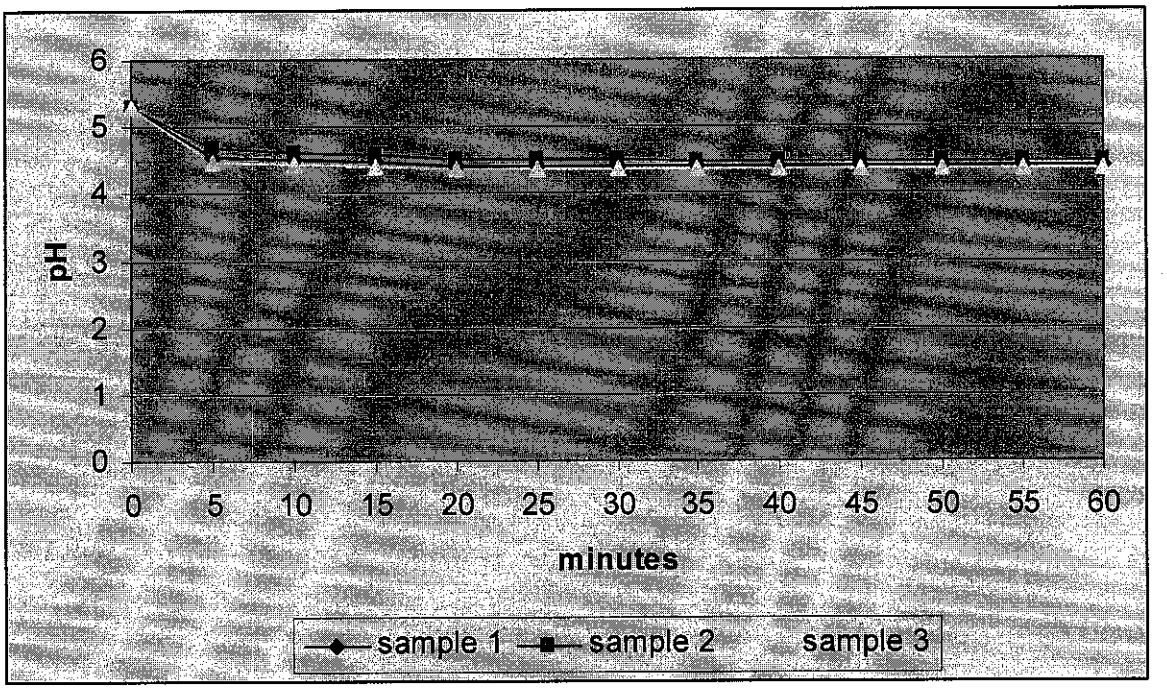


Figure 8: Graph of pH vs. time for Fenton oxidation

From the entire graph shown earlier, the effect of pH to the reaction is important. The optimal pH where the reaction occurs is at pH 4. According to the theory, the optimal pH is at around 3 to 6 (Lenntech, 2003). This experiment results comply with the theory.

This inflection is caused by the $FeSO_4$ catalyst which typically contains residual H_2SO_4. Then the decrease was also contributed from addition of H_2O_2 and it continues gradually drop at rate which is largely dependent on catalyst concentration. This drop in pH is attributed to the fragmenting of organic material into organic acids.

As what we done in the experiment, the pH often monitored in previous study to ensure that the reaction is progressing as planned. If there are no decreases in pH, it means that

the reaction is inhibited and that a potentially hazardous build up of H_2O_2 is occurring with the reaction mixture.

In highly concentrated stream such as more than 10 g/L COD value, the oxidation steps need to be perform and the pH has to be readjust to pH 4-5 after each steps to prevent the low pH inhibiting the reaction.

Percentage of reduction of the COD value was concluded in table 10 below:

Table 10: Percentage of reduction of the COD value after Fenton process

Ratio of Fe: H_2O_2	Average COD value (mg/L)	Percentage reduction
1:5	280	8.20%
1:10	246	19.34%
1:15	197	35.41%
1:20	149	51.15%
1:25	114	62.62%

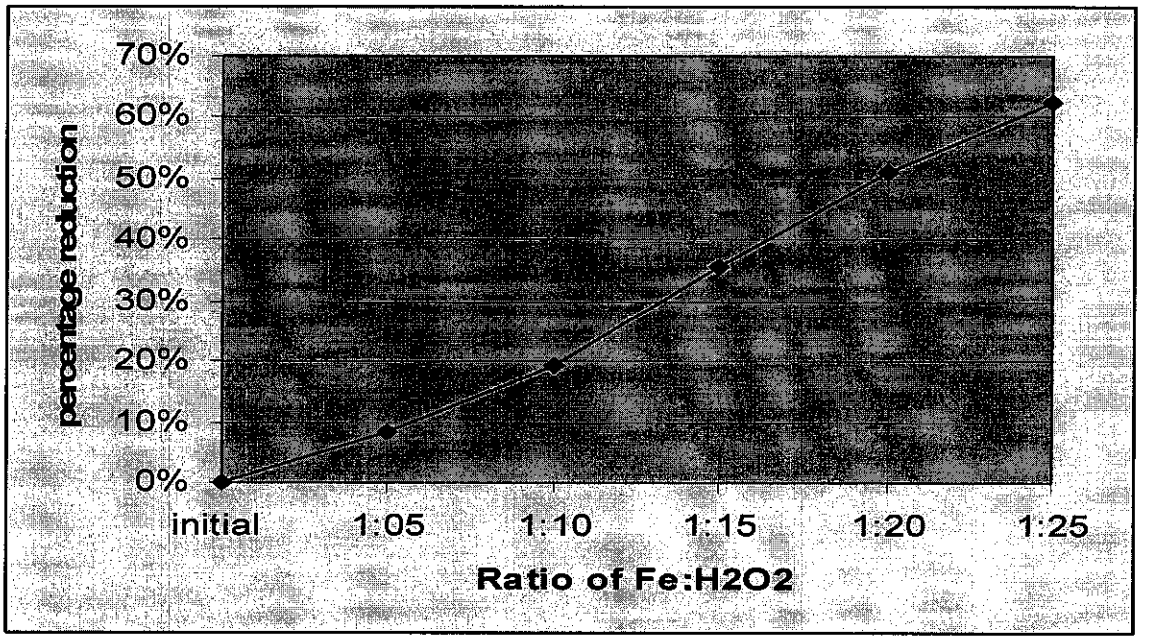


Figure 9: Graph of percentage reduction vs. ratio of Fe: H_2O_2

The experiments show an increment of the percentage reduction of the COD value after Fenton process. The more the H_2O_2 added according to the ratio, the more efficient it reduces the COD concentration in the wastewater.

The trend of the percentage reduction increment can be seen from figure 9. The graph shows that the reduction is getting higher as the ratio getting bigger. Although this experiment are not up to 100% reduction of COD value and the final COD value is not under 100 mg/L, we can still proceeds to ratio more than 1: 25 to obtain a more good results.

4.2.2 Changes in color and sludge generation

Another analysis and observation done on this experiment is the changes in color of the wastewater. It is important to observe and monitored the changes in color of the wastewater before and after experiments.

Figure shown below are the results of the color changes before the experiments:

Figure 10: Wastewater's color before experiments

If we see the above figure, the color of the wastewater is quite dark red in color. This can be said that the effluent is in high concentration of organic dyes. High concentration of organic dyes means that the content of organic dyes is quite high, thus it makes the color are quite dark red. Next figures show the results of the color changes for each ratio after the experiment.

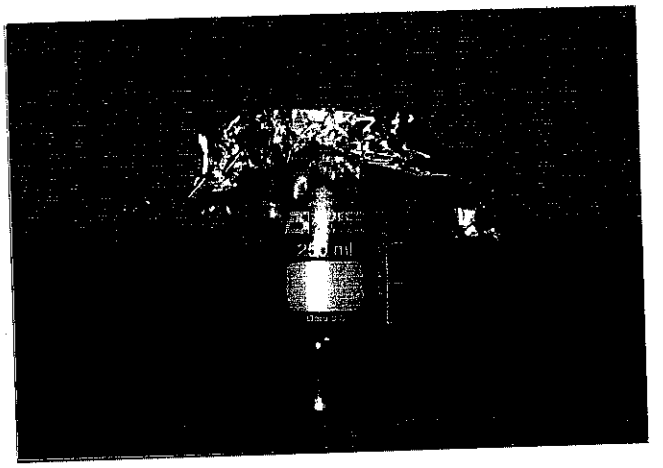


Figure 11: Ratio of 1:5

Figure 12: Ratio of 1:10 and 1: 15

Figure 13: Ratio of 1:20 and 1: 25

The data shown in Table 11 to table 15 are the results obtained from photo-Fenton's process experiment, for ratio (Fe: H_2O_2) of 1:5 to 1:25 which was conducted under light radiation environment.

The experiment for photo-Fenton was begun at initial pH of approximately 5. At first, the initial pH of the wastewater was detected at pH 11 and for sure, it is basic side. The requirement for carrying out the experiment is the initial pH has to be at around pH 5. The pH was adjusted to pH 5 before the experimental procedure was carried out.

The temperature was set as usual at 30.0 degC for certain reason which will be discussed later. The pH was monitored to see the trend of the decreasing pH. It is also to ensure that the pH decreasing based on the theory applied. If the pH decrement is comply with the theory, and then it means that the reaction is progressing as planned.

After the experiments are settle at 60 minutes, the pH of the samples are mostly maintained. Although it have some decrement, the decrease in pH in not obvious and can be assumed it decrease gradually and begin to be constant after some time. For all the graphs which discussed earlier and after, the pH of the sample at 60 minute is constant starting from minute 15 to 20. This is the best pH where the reaction can take place and the pH is around 4.

If we refer to figure 14, Photo-Fenton experiment show a more decreasing pattern in pH compared to Fenton experiment. This is due to the reasons stated earlier why we use light radiation for photo-Fenton experiment. The pH decrease more and approaching pH 4. This is due to the addition of $FeSO_4$ and H_2O_2, and helped by the light radiation where it produces additional hydroxyl radicals and the recovery of Fe (II) needed in Fenton reaction. The trend of decreasing pH is similar to other ratio as well.

The same explanation applied for the other results. The only difference is based on their initial pH adjustment which is not a major problem, since we assume the initial pH id adjusted at around 5.

Table 11: Results for photo-Fenton experiment with ratio (Fe: H_2O_2) of 1:5

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.24	29.5	5.24	29.5	5.25	29.5
5	4.22	29.5	4.27	29.5	4.23	29.5
10	4.18	30.0	4.23	30.0	4.16	30.0
15	4.13	30.0	4.16	30.0	4.14	30.0
20	4.12	30.0	4.16	30.0	4.14	30.0
25	4.12	30.0	4.16	30.0	4.14	30.0
30	4.12	30.0	4.15	30.0	4.14	30.0
35	4.12	30.0	4.15	30.0	4.14	30.0
40	4.11	30.0	4.15	30.0	4.13	30.0
45	4.11	30.0	4.15	30.0	4.13	30.0
50	4.11	30.0	4.14	30.0	4.13	30.0
55	4.11	30.5	4.14	30.5	4.13	30.5
60	4.09	30.5	4.14	30.5	4.11	30.5
COD	247		275		252	
Average COD	258					

Table 12: Results for photo-Fenton experiment with ratio (Fe: H_2O_2) of 1:10

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.28	28.5	5.28	28.5	5.28	28.5
5	4.35	28.5	4.48	28.5	4.29	28.5
10	4.31	28.5	4.41	28.5	4.24	28.5
15	4.27	29.0	4.37	29.0	4.20	29.0
20	4.22	29.5	4.30	29.5	4.16	29.5
25	4.21	30.0	4.30	30.0	4.16	30.0
30	4.21	30.0	4.30	30.0	4.16	30.0
35	4.21	29.5	4.29	29.5	4.16	29.5
40	4.20	30.0	4.29	30.0	4.15	30.0
45	4.20	30.0	4.29	30.0	4.15	30.0
50	4.20	30.0	4.29	30.0	4.15	30.0
55	4.20	30.0	4.28	30.0	4.15	30.0
60	4.19	30.0	4.28	30.0	4.15	30.0
COD	196		213		188	
Average COD	199					

Table 13: Results for photo-Fenton experiment with ratio (Fe: H_2O_2) of 1:15

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.23	29.5	5.23	29.5	5.23	29.5
5	4.19	29.5	4.24	29.5	4.18	29.5
10	4.15	29.5	4.20	29.5	4.15	29.5
15	4.10	29.5	4.15	29.5	4.11	29.5
20	4.07	30.0	4.12	30.0	4.08	30.0
25	4.05	30.0	4.12	30.0	4.04	30.0
30	4.05	29.5	4.12	29.5	4.04	29.5
35	4.05	30.0	4.11	30.0	4.04	30.0
40	4.05	30.0	4.11	30.0	4.04	30.0
45	4.04	30.0	4.11	30.0	4.03	30.0
50	4.04	30.0	4.11	30.0	4.03	30.0
55	4.04	30.0	4.10	30.0	4.03	30.0
60	4.04	30.0	4.10	30.0	4.03	30.0
COD	161		158		149	
Average COD	156					

Table 14: Results for photo-Fenton experiment with ratio (Fe: H_2O_2) of 1:20

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.27	29.5	5.27	29.5	5.27	29.5
5	4.20	29.5	4.21	29.5	4.20	29.5
10	4.16	30.0	4.18	30.0	4.17	30.0
15	4.11	30.0	4.13	30.0	4.15	30.0
20	4.07	30.0	4.09	30.0	4.10	30.0
25	4.04	30.0	4.05	30.0	4.09	30.0
30	4.03	30.0	4.05	30.0	4.09	30.0
35	4.03	30.0	4.05	30.0	4.09	30.0
40	4.03	30.0	4.04	30.0	4.08	30.0
45	4.02	30.0	4.04	30.0	4.08	30.0
50	4.02	30.0	4.04	30.0	4.08	30.0
55	4.02	30.0	4.04	30.0	4.08	30.0
60	4.02	30.0	4.03	30.0	4.08	30.0
COD	117		111		138	
Average COD	122					

Table 15: Results for photo-Fenton experiment with ratio (Fe: H_2O_2) of 1:25

Minutes	Sample 1		Sample 2		Sample 3	
	pH	T (°C)	pH	T (°C)	pH	T (°C)
0	5.20	29.0	5.20	29.0	5.20	29.0
5	4.17	29.0	4.21	29.0	4.19	29.0
10	4.13	29.5	4.17	29.5	4.15	29.5
15	4.10	29.5	4.15	29.5	4.12	29.5
20	4.06	29.5	4.11	29.5	4.09	29.5
25	4.04	30.0	4.08	30.0	4.05	30.0
30	4.03	30.0	4.08	30.0	4.05	30.0
35	4.03	30.0	4.08	30.0	4.05	30.0
40	4.03	30.0	4.07	30.0	4.05	30.0
45	4.03	30.0	4.07	30.0	4.04	30.0
50	4.02	30.0	4.07	30.0	4.04	30.0
55	4.02	30.0	4.07	30.0	4.04	30.0
60	4.02	30.0	4.07	30.0	4.04	30.0
COD	95		91		90	
Average COD	92					

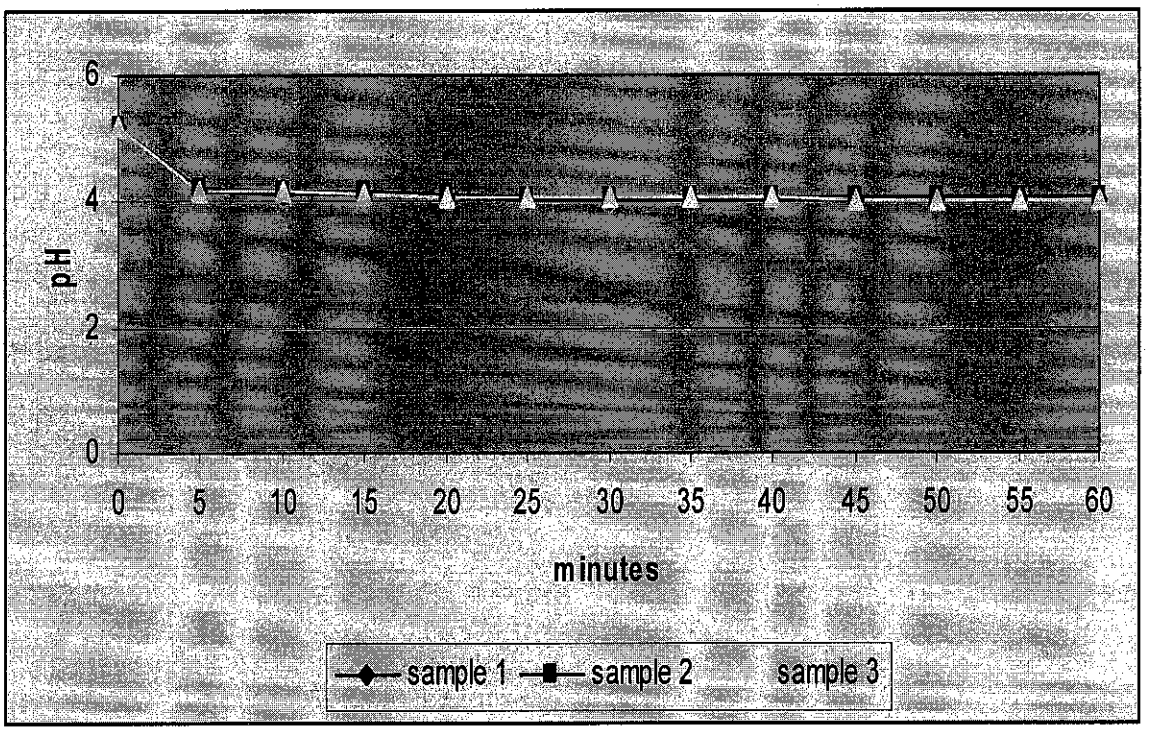


Figure 14: Graph of pH vs. time for photo-Fenton oxidation

Percentage of reduction of the COD value was concluded in table 10 below:

Table 16: Percentage of reduction of the COD value after photo-Fenton process

Ratio of Fe: H_2O_2	Average COD value (mg/L)	Percentage reduction
1:5	258	15.41%
1:10	199	34.75%
1:15	156	48.85%
1:20	122	60.00%
1:25	92	70.00%

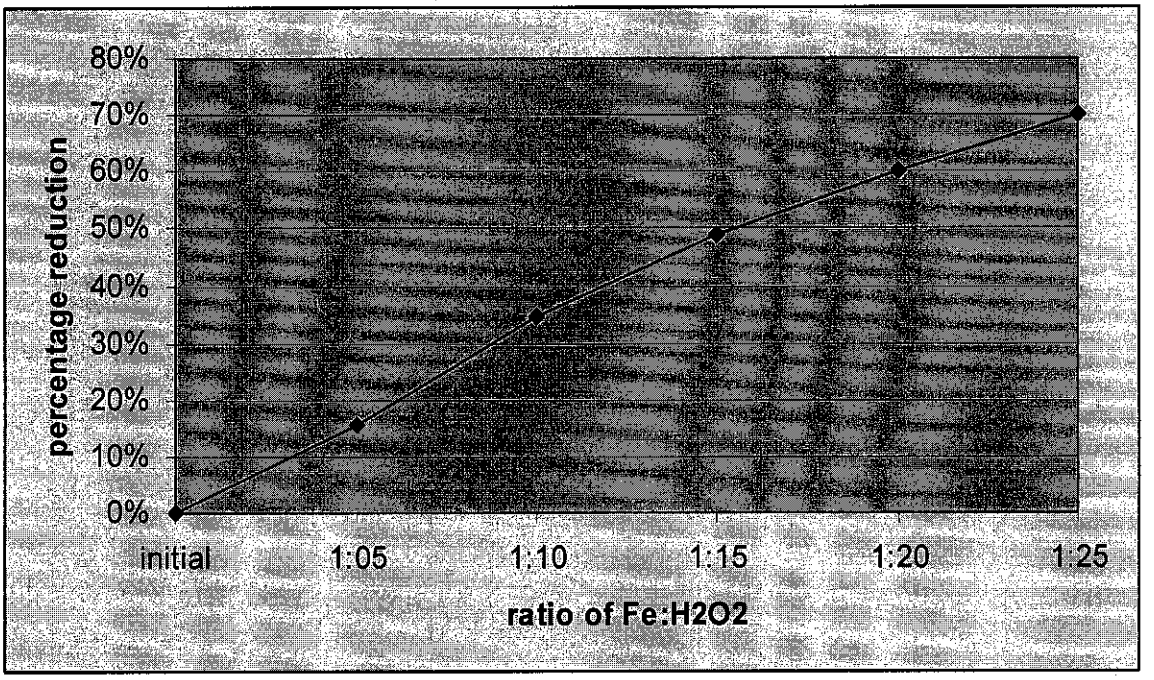


Figure 15: Graph of percentage reduction vs. ratio of Fe: H_2O_2

The experiments show an increment of the percentage reduction of the COD value after Fenton process. The more the H_2O_2 added according to the ratio, the more efficient it reduces the COD concentration in the wastewater.

The trend of the percentage reduction increment can be seen from figure 15. The graph shows that the reduction is getting higher as the ratio getting bigger. Although this experiment are not up to 100% reduction of COD value, but the reduction is already achieved the objective where we are able to reduce the COD value below than 100 mg/L.

4.3.2 Changes in color and sludge generation

The color analysis for photo-Fenton is similar to Fenton process. Figure shown below are the results of the color changes before the experiments:

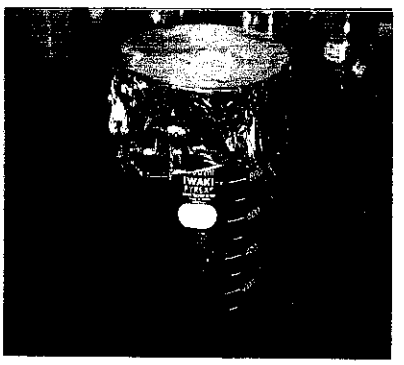


Figure 16: Wastewater's color before experiments

If we see the above figure, the color of the wastewater is quite dark red in color. This can be said that the effluent is in high concentration of organic dyes. High concentration of organic dyes means that the content of organic dyes is quite high, thus it makes the color are quite dark red. Next figures show the results of the color changes for each ratio after the experiment.

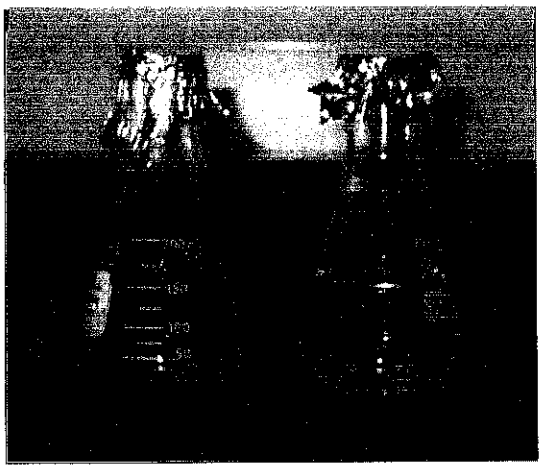


Figure 17: Ratio of 1: 5 and 1:10

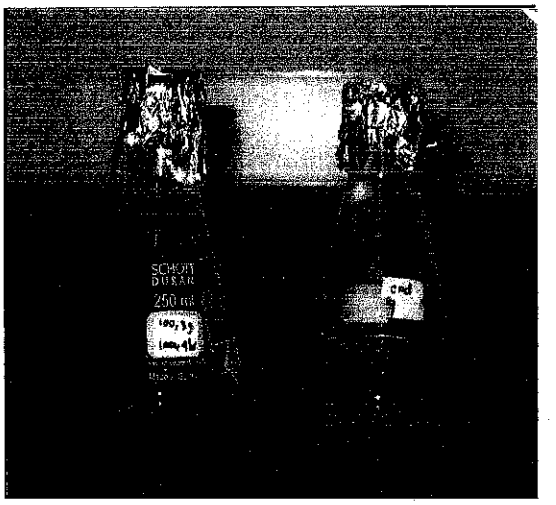


Figure 18: Ratio of 1: 15 and 1:20

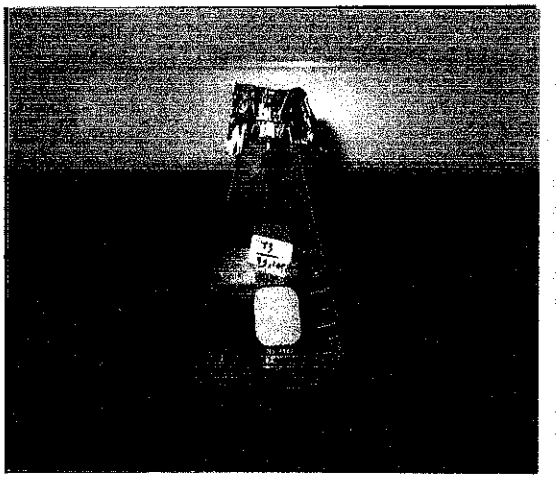


Figure 19: Ratio of 1: 25

4.4 Final results for Fenton and photo-Fenton experiments

Table 17: Final results of COD value (average) after the experiment

Ratio of Fe:H_2O_2	Average COD value (mg/L)	
	Fenton	Photo-Fenton
1:5	280	258
1:10	246	199
1:15	197	156
1:20	149	122
1:25	114	92

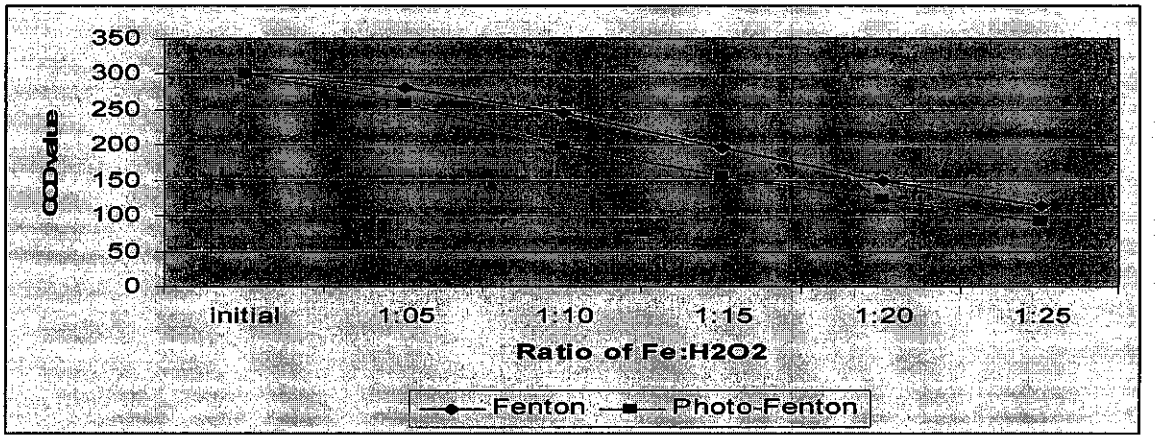


Figure 20: Graph of COD value vs. ratio of Fe: H_2O_2

4. 5 Discussion and findings on the project

4.5.1 Effect of pH

As expected, the process based on Fenton's reagent is a pH dependant processes. However, each reaction has its optimum performance at different pH values. Based on the results obtained, Fenton's process is a pH independent process where we can see that the comparison between pH after addition of $FeSO_4$ and H_2O_2 for both experiment shows that pH for photo-Fenton's process decrement are more than Fenton's process.

A very acidic or neutral basic media slows down the process. The low activity detected for high pH values can be explained by the formation and precipitation of $Fe(OH)_3$, a

process that hamper the development of photo-Fenton reactions. Decrease of activity for pH values below the optimum is understandable taking into account that Fe (III) forms different complex species in solution and the quantum yield of light absorption by Fe(III) is directly depending on the specific species responsible for the absorption.

Theoretically, the optimum pH for the reaction to take place is around 3-5. The most ideal pH for reaction is agreed to be around pH 4. This was applied in the experiments where most of the pH after addition of the reagent drop to pH 4 and react to remove the organic dyes contained in the wastewater.

The first and second drops on pH (refer to figure 8 and figure 14) which happens mostly to all the experiments is a result of addition of $FeSO_4$ catalyst which contains residual H_2SO_4. The second drop which was not very clear in the graphs are due to the addition of H_2O_2 and the pH values continues gradually at rate which is largely dependant on the catalyst concentration.

4.5.2 Effect of temperature

In any case, temperature is a key parameter that has to be taken into account, especially for those applications where COD removal can be increased. The rate of reaction with Fenton's reagent and photo-Fenton's reagent increase with the increasing of the temperature. However, if the temperature of the process is increase above 40-50°C, the efficiency of H_2O_2 utilization declines. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. As a practical matter, which was applied in the experiment, temperature around 20-40°C is the most ideal and commercial.

For certain purposes, blank experiment were conducted to choose the best temperature for the process to take place. A blank experiment with different temperature at 20°C and

30°C for Fenton's process were carried out. At the end of the experiment, the sample with temperature at 30°C lost more color content than sample with temperature at 20°C.

Thus, it concludes that temperature around 30°C is the most ideal temperature for the reaction to take place.

4.5.3 Effect of reaction time

Although the experiment results were showing that it was carried out in 60 minutes, the settling time of the experiment was not 60 minutes or 1 hour. The settling time is more than 1 hour for this experiment. The COD value was taken after 60 minutes and one day settling time. The sample with one day settling time shows a more decreasing amount in COD value than the sample with 60 minutes settling time.

Actually, the time needed to complete a Fenton and photo-Fenton reaction will depend on many variables, it is most likely because of the catalyst dose and wastewater strength. Determining the completion of the reaction may prove troublesome. The presence of residual H_2O_2 will interfere with many wastewater analyses. Residual H_2O_2 may be removed by raising the pH to 7-10, or by neutralizing with bisulfite solution. Often, observing color changes can used up as the reaction reaches completion.

4.5.4 Effect of iron type

In these experiments, Fe^{2+} salts are used to catalyze the reaction together with H_2O_2. In fact, the type of salts whether it is Fe^{2+} or Fe^{3+} is not important. This is due to the catalytic cycle begins quickly if H_2O_2 and organics material are in abundance. However, if the Fenton's reagent used is in low doses, some research suggests that it is best if using ferrous iron. (Lenntech, 2003)

By raising the pH, the iron is possible to be recycled again. $FeSO_4$ in the experiment are as a catalyst and clearly a limiting chemical. This is due to the increasing amount of

H_2O_2 and thus the Fe^{2+} becoming a limiting chemical. The reaction is limited because of the concentration of iron catalyst which generally affect the rate of ·OH generation, and less so by the specific wastewater being treated.

4.5.5 Effect of H_2O_2 concentration

Concentration of H_2O_2 is one of the factor which helps to increase the reaction rate to be faster and effective. As we can see from the results shown, as the concentration of the H_2O_2 increases, the COD value also decreases and the drop in pH after addition of the reagent becomes bigger than previous concentration. A little or no toxicity happen with the decreasing amount of the COD value until a threshold is attained. Thus, increasing the concentration of the H_2O_2 can rapidly decrease the wastewater toxicity.

4.5.6 Effect of light radiation

Light radiation helps to improve the reaction to a greater reduction in COD value and color diminishing. The intensity and the wavelengths emitted by the light source are condition when trying to describe the participation of the light driven reaction. It is especially interesting, from the application point of view, the possibility of using solar light.

It is difficult to find an explanation for such a behavior a type of light source can affect the reaction, but it seems that an intense irradiation favors the fast exhaustion of H_2O_2 through non efficient reactions while mild irradiation consumes less oxidant in parallel and undesired photo chemical reactions.

Difficulties on maintaining the solar irradiation at a constant temperature could also be taken into account when trying to find an explanation for such an unexpected behavior.

4.5.7 Effect of experiment procedure

Adding the H_2O_2 slowly and drop by drop can help in order to control the increasing of the pH and the temperature during the reaction. Thus, it is better to complete the reaction step by step with a continuous adjustment. It has to be considered also the degree of the milipipette mouth used is adjusted straight to the solution in the glass ware. If not, the reagent such as H_2O_2 will spill on the wall of the glass ware and not enough dose of the reagent will affect the experiment.

The effectiveness of the equipment must be taken into account too. The calibration for equipment can help to get a more precise reading such as the DR4000 spectrophotometer and the pH sensor.

4.5.8 Comparison on both processes

If we refer to figure 20, it is clearly shown photo Fenton process reduces the COD value faster than Fenton process. It can be seen that at each ratio, the COD value of photo-Fenton process is lesser than Fenton process. It is also shown that photo-Fenton process react faster with the availability of the light source which enhances the photo-reduction reaction.

4.5.9 Color analysis and sludge generation

The color of the wastewater before the experiment is pictured on figure 10 and figure 16. The color is quite dark due to the type of the dyes used. The wastewater also have odor like resin and the pH are also high, around pH 11. After the Fenton and photo-Fenton experiment, the color become brownish and a little sludge were formed at the bottom of the glassware. This shows that Fenton's reagent based treatment not only able to reduce the COD value of the wastewater, but also able to diminish the color content, especially the organic dye content. The brownish color means that almost of the organic dyes were removed due to same results were found from other research of the same treatment. Thus, it is clearly proved that the Fenton reagent based treatment is applicable to remove the organic dyes in the wastewater.

The odor also totally diminished unlike its earlier odor. The odor is mostly caused by the content of the organic dyes in the wastewater. Sludge generation still occur but in very small amounts. This small amount was generated in a lab scale, and if it is to be generated in plant scale, the sludge will be surely generated in a large amount. Some of the technologies nowadays burn the sludge in the incinerator to produce energy. This is one of the steps to diminish the sludge produces by the treatment.

4.5.10 Important point of the discussion

Below are the summary of the points from the discussion:

- It is clearly shown that photo-Fenton process reduces the COD content in waste water efficiently and faster.
- Initial pH of waste water before experiment is crucial for the reaction to happen.
- Temperature at around 20 – 40 °C also helps to boost the reaction's efficiency.
- Adding H_2O_2 slowly into the samples during the experiment also helps to increase the reaction's efficiency.
- Color of the waste water was diminished after the experiment, means that the dye is totally amended by the Fenton and photo-Fenton process.
- The advantages of Fenton's reagent based treatment are effective decolourization of both soluble and insoluble dyes.
- Sludge generated although in small quantities.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

- Photo-Fenton process works better than Fenton process.

- Fenton reagent based process can effectively decolorize the dyes and reduce the content of the chemical oxygen demand (COD) value in textile effluents.

- pH, temperature, and ratio of the reagent are the important parameters to be considered in the process.

5.2 Recommendation

- Variety of H_2O_2 concentration and $FeSO_4$ dose should be applied in the future experiments.

- Equipments such as spectrophotometer for COD reading should be calibrated for accuracy.

- Condition of dark environment and under light source should be applied carefully and without outsider factors.

REFERENCE

Banat, McMullan, Meehan, Kirby, Nigam, Smyth, Marchant, 1999, *Microbial decolourization of textile dyes present in textiles industries effluent*, Proceedings of the Industrial Waste Technical Conference, Indianapolis, USA.

Davis, Gainer, O'Neal, G. and Wu, 1994, *Photo catalytic decolourization of wastewater dyes*, Water Environment.

E.G Solozhenko, N.M. Soboleva, and V.V. Goncharuk, 1995, *Decolourization of Azodye Solutions by Fenton's Oxidation*, Institute of Colloidal Chemistry and Water Chemistry, Ukrainian Academy of Sciences.

Elsevier, www.elsevier.com.,

Eco.web, www.eco-web.com

Francis A. Carey, 2000, Organic Chemistry, International Edition, Fourth Edition, McGraw Hill Publications.

Final Year Project Guidelines, Semester January 2004, School of Chemical Engineering, University Technology of PETRONAS.

HACH (program 8000), 1999, *Procedure for Oxygen Demand, Chemical*, HACH Company.

HACH (program 8025), 1999, *Procedure for Color, True, and Apparent*, HACH Company.

H2O2.com, www.h2o2.com/applications/industrialwastewater/fentonsreagent.html

Ira N. Levine, 2002, Physical Chemistry, Fifth Edition, McGraw Hill Publications.

Kumar, M.N.V.R., Sridhari, T.R. Bhavani, K.D. Dutta, P.K., 1998, *Trends in color removal from textile mill effluents*, Colorage.

Lenntech, www.lenntech.com/Fenton-reaction.com.htm

M.A. Haroun and A. Idris, *Review on Current Treatment Technologies of Textile Dyes Removal with a Proposed Alternative*, Department of Chemical and Environmental Engineering, Universiti Putra Malaysia.

Montserrat Perez, Francesc Torrades, Xavier Domenech, Jose Peral, 2001, *Fenton and photo-Fenton Oxidation of Textile Effluents*, Department of Chemical Engineering, University Polytechnic de Catalunya, Barcelona, Spain.

Octave Levenspiel, 1999, Chemical Reaction Engineering, Third Edition, John Wiley and Sons, Inc.

Poots, V.J.P., McKay, J.J., 1976, *The removal of acid dye from effluent using natural adsorbents- Peat*, Water Res.

R. Aplin and T.D.Waite, 2000, *Comparison of three advanced oxidation process for degradation of textile dyes*, Water Science and Technology, Volume 42, IWA Publishing.

Raghavacharya, C., 1997, *Color removal from industrial effluents- a comparative review of available technologies*, Chemical Engineering World.

Reddy, C.A., 1995, *The potential for white-rot fungi in the treatment of pollutants*, Curr.Opt.Biotechnol.

Reeves, P., Ohlhausen, R., Sloan, D., Pamplin, K Scoggins, 1992, *Photo catalytic destruction of organic dyes in aqueous titanium oxide suspensions using concentrated simulated and natural solar energy*, Solar Energy.

Strickland, A.F, and Perkins, 1995, *Decolourization of continuous dyeing wastewater*, Dyes pigments.

W. Wong, T.T. Teng and N.A. Nik Norulaini, "Removal of Disperse Dye and Reactive Dye by Coagulation- Flocculation Method", School of Industrial Technology, Universiti Sains Malaysia.

Xu, Y., Lebrun, R.E., 1999, *Treatment of Textile dye plant effluent by nanofiltration membrane*, Separation Science Technology.